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(21) International Application Number: PCT/US98/01972 (22) International Filing Date: 2 February 1998 (02.02.98) (30) Priority Data: 08/800,676 14 February 1997 (14.02.97) US (71) Applicant: RAYCHEM CORPORATION [US/US]; 300 Constitution Drive, Mail Stop 120/6600, Menlo Park, CA 94025 (US). (72) Inventor: SUNSHINE, Steven; 2515 Lorain Road, San Marino, CA 94070 (US). (74) Agents: CHAO, Yuan et al.; Raychem Corporation, Intellectual Property Law Dept., 300 Constitution Drive, Mail Stop 120/6600, Menlo Park, CA 94025 (US).		(81) Designated States: CA, JP, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: METHOD FOR EXTRACTING GASES DISSOLVED IN A LIQUID (57) Abstract Gases dissolved in a liquid such as transformer oil are separated from the liquid with a separation cell having a permselective membrane made from a perfluoro-2,2-dimethyl-1,3-dioxole polymer.		

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METHOD FOR EXTRACTING GASES DISSOLVED IN A LIQUID

TECHNICAL FIELD OF THE INVENTION

This invention relates to a method for extracting gases dissolved in a liquid.

BACKGROUND OF THE INVENTION

5 Sometimes it is desirable to extract gases from an analyte liquid in which they are dissolved, to enable their qualitative or quantitative analysis. Such a situation exists in power transformers, in which the transformer oil may accumulate dissolved carbon monoxide, carbon dioxide, water vapor, and low molecular weight hydrocarbons such as methane, ethane, ethylene, and acetylene. The identity of an accumulated gas, its
10 concentration, and rate of accumulation can provide valuable diagnostic information about the transformer's health, alerting a utility company to a fault which can lead to destructive failure of the transformer if not corrected.

Various separation techniques have been proposed, ranging from gas chromatography to membrane systems. Membrane systems are desirable because they offer
15 simplicity in design and require less maintenance. However, a frequent problem with membranes is the separation rate. If the separation rate is too slow, then the ability to perform "real-time" separation and analysis is compromised.

BRIEF SUMMARY OF THE INVENTION

The present invention provides a membrane-based method which is improved over
20 prior art methods speed-wise. Accordingly, there is provided a method of extracting dissolved gas from a gas-containing liquid, comprising the steps of

- (a) providing a separation cell having a permselective membrane comprising an amorphous perfluoro-2,2-dimethyl-1,3-dioxole polymer, the membrane partitioning the cell into a feed chamber and a permeate chamber;

- (b) introducing into the feed chamber a gas-containing liquid towards which the membrane is substantially impermeable, the gas-containing liquid at least one gas dissolved therein;
- (c) permitting the at least one gas to permeate across the membrane from the feed chamber to the permeate chamber; and
- (d) removing the at least one gas from the permeate chamber.

BRIEF DESCRIPTION OF THE DRAWING(S)

Fig. 1 shows a preferred embodiment in which the membrane is a composite membrane.

Fig. 2 shows a mechanical support for the membrane.

Fig. 3 shows an apparatus for practicing this invention.

Figs. 4a and 4b show additional apparatus for practicing this invention.

Herein, reference numerals repeated from one figure to another denote the same or like elements.

DETAILED DESCRIPTION OF THE INVENTION

Amorphous polymers of perfluoro-2,2-dimethyl-1,3-dioxole ("PFDD") have been used as permselective membranes for gas separation or enrichment processes, in which a component gas in a gas mixture is separated from or enriched with respect to the other component gases. However, in such processes the membrane need only be differentially permeable to the various component gases — it need not be impermeable to one or more of mixture components.

PFDD polymers have not been employed as the base material in permselective membranes for the separation of gases from a gas-containing liquid, an application which requires the membrane should be substantially impermeable to the liquid. Passage of the liquid through to the permeate chamber can interfere with the equipment used to transport or analyze the permeate gases or with the analytical method per se, for example preventing the use of infrared techniques. I have discovered that PFDD polymers unexpectedly offer

an advantageous combination of high permeability to gases dissolved in a liquid and impermeability to the liquid.

As used herein, the terms "PFDD polymer" and "perfluoro-2,2-dimethyl-1,3-dioxole polymer" mean the homopolymer and copolymers of perfluoro-2,2-dimethyl-1,3-dioxole. PFDD polymers suitable for this invention are disclosed in Squire, US 4,948,851
5 (1990); Squire, US 4,975,505 (1990); Squire, US 4,999,248 (1991); Squire, US 5,006,382 (1991); and Nemser et al., US 5,051,114 (1991); the disclosures of which are incorporated herein by reference. In the instance of copolymers, PFDD is copolymerized with at least one comonomer selected from the group consisting of tetrafluoroethylene, perfluoromethyl
10 vinyl ether, vinylidene fluoride, and chlorotrifluoroethylene with PFDD constituting between 65 and 99 mole % of the copolymer. The PFDD polymer preferably has a glass transition temperature (T_g) between 140 and 240 °C. PFDD polymers are available under the tradename Teflon AF from E.I. Du Pont de Nemours and Company, Wilmington, Delaware, in grades such as 1600 and 2400, having T_g 's of 160 and 240 °C, respectively.

15 While the membrane may be an unsupported membrane of PFDD polymer, it may be desirable to minimize the thickness of the membrane to maximize the diffusion rate of the gases. Then, the membrane can beneficially be supported, for example on a porous support of, for example, vinylidene difluoride homopolymer or copolymer (collectively "PVDF polymer"), to form a composite membrane having improved ruggedness without
20 sacrificing diffusion rates. Such a membrane is shown in partial cross-section in Fig. 1. Composite membrane 1 includes a thin layer 2 of PFDD polymer supported by a supporting material 3 made of PVDF polymer. Supporting material 3 is porous, having pores 4. In use, layer 2 should face the feed chamber, to avoid having the liquid filling up the void volume of support material 3. With a composite construction, layer 2 can be made very
25 thin, as thin as 0.5-6 μm , by solvent casting of PFDD polymer onto supporting material 3. If coatings thicker than 0.5-6 μm are desired, multiple coatings may be applied. While multiple coating may undesirably thicken the PFDD polymer layer, it offers the advantage of safeguarding against pinhole defects, as might occur if only a single coating is used.

Techniques for the preparation of composite membrane 1 are disclosed in Baker, US
30 4,553,983 (1985); Blume et al., US 4,990,255 (1991); Blume et al., US 4,931,181 (1990);

Blume et al., US 4,963,165 (1990); Castro et al., US 5,049,167 (1991); Bowser, US 5,116,650 (1992); Toy et al., US 5,281,255 (1994); and Blume et al., US 5,085,775 (1992); the disclosures of each of which are incorporated herein by reference. Except for the Bowser patent, the preceding patents are all assigned to Membrane Technology and Research, Inc., of Menlo Park, California, from whom the inventor was able to obtain suitable PFDD polymer composite membranes.

The permselective membrane permits the dissolved gas(es) in the gas-containing liquid to diffuse thereacross to the permeate chamber, while being substantially impermeable to the gas-containing liquid and retaining it in the feed chamber. By "substantially impermeable," it is meant that insufficient gas-containing liquid passes through to the permeate chamber to interfere with the functions of transporting the extracted gas, separating it into its constituent components, and/or its analysis (with or without prior separation into constituent components).

The membrane (whether composite or otherwise) may additionally be mechanically supported, for example by a wire mesh. Fig. 2 shows a membrane holder 10 adapted for supporting a circularly shaped membrane (not shown), comprising a circular perforated base 12 (e.g., a perforated metal plate or a wire mesh) having around its periphery a rubber edging 14. In use, the membrane is sandwiched between a pair of membrane holders 10, with edgings 14 gripping the edges of the membrane without damaging it. Edgings 14 also provide a seal between the feed and permeate chambers and prevent liquid from leaking from one side to the other around the edges of the membrane. It is understood that the membrane need not necessarily be circular in shape, such shape being cited here only for purposes of illustration.

An apparatus for practicing this invention is shown schematically in Fig. 3. Separation cell 20 has a feed chamber 22 and a permeate chamber 24, separated from each other by a permselective membrane 26. When feed chamber 22 contains a liquid 29 containing dissolved therein one or more gases 30, gases 30 diffuse across membrane 26, but liquid 29 is retained. (While it is preferred that feed chamber 22 be substantially filled with liquid 29, this is not essential; partial filling is permissible.) The result is that permeate chamber contains only gases 30. The relative proportions of gases 30 on the

permeate chamber (where there is more than one gas dissolved in liquid 29) will depend on their relative proportions dissolved in liquid 29 on the feed chamber and their respective distribution (Ostwald) coefficients. From a measurement of the relative amounts of gases 30 in the permeate chamber and a knowledge of their distribution coefficients (information which is either already known or readily ascertainable for most common gases), one can back-calculate the concentrations of the gases in liquid 29. Feed chamber 22 can be filled and emptied via inlets and outlets controlled by valves 28a and 28b. To prevent the build-up of depletion layers as the diffusion process takes place, it is preferable to provide some circulation of liquid 29. Gases 30 on permeate chamber 24 can be transported to a measurement apparatus via an outlet controlled by valve 28d. Optionally, a carrier gas can be introduced via an inlet controlled by valve 28c to facilitate transport. The aforementioned inlets and outlets are also useful for occasionally purging the feed or the permeate chamber, as desirable for repairs, maintenance or calibration. A preferred apparatus for performing the various aforementioned functions is described in US Patent Application of Mattis et al., Serial No. 08/798,283, filed Feb. 14, 1997, entitled "Apparatus for Extracting a Gas from a Liquid and Delivering the Gas to a Collection Station," the disclosure of which is incorporated herein by reference.

Fig. 4a shows an alternative separation cell 31, in which the PFDD polymer membrane is in the form of a serpentine hollow tube 34. The interior of tube 34 serves as the permeate chamber, while the volume of cell 31 external to tube 34 serves as feed chamber 32. It is to be understood that more than one tube 34 may be present, with only one shown here for simplicity.

Fig. 4b shows yet another alternative separation cell 41, in which the PFDD polymer membrane is in the form of a bundle of hollow fibers or tubes 44 (three shown). Again, the volume of cell 41 external to tubes 44 serves as feed chamber 42.

No particular pressure needs to be applied to the feed chamber to effect separation. However, it may be desirable to apply a vacuum or a positive pressure to either the feed or the permeate chamber at one time or another, in the course of performing a function such as transport, purging or cleaning. Then, the membrane can experience a pressure ranging from about -14 psi (a vacuum) to +40 psi. Thus, it is desirable that the permselective membrane

(supported by a composite structure or a mechanical support, as described above) be able to withstand such pressures without rupturing.

This invention is especially useful for the monitoring dissolved gases which accumulate in a power transformer's fluid as the transformer ages. The oil in a transformer is typically either a hydrocarbon oil or a silicone oil. Faults in a transformer, such as a hot spot or an arc, cause localized deterioration of the oil and the generation of gases such as carbon monoxide, carbon dioxide, hydrogen, water vapor, methane, ethane, ethylene, and acetylene, or combinations thereof. The identity, concentration, and build-up rate of these gases is valuable for diagnosing the state of a transformer. A number of devices for providing such monitoring capability have been proposed, such as disclosed in Kurz et al., US 4,058,373 (1977); Morgan, US 4,112,737 (1978); Sakai et al., US 4,444,040 (1984); Sakai et al., US 4,502,320 (1985); Poyser et al., US 4,654,806 (1987); Claiborne et al., US 4,890,478 (1990); Abe et al., US 5,258,310 (1993); Spicar, US 5,339,672 (1994); Slemon et al., US 5,400,641 (1995); and Muhlwitz et al., WO 95/28626 (1995). While some devices do not require the separation of the gases from the oil, generally such separation is a prerequisite to analysis. The present invention is especially useful for use in a transformer monitor as described in US Patent Application of Sunshine et al., Serial No. 08/800,678, filed Feb. 14, 1997, entitled "System for Measuring Gases Dissolved in a Liquid," the disclosure of which is incorporated herein by reference. While the invention is most useful where plural gases are involved, it also can be used where the liquid contains only a single dissolved gas.

An advantage of membranes made from PFDD polymers is that they are very permeable to the gases of interest in transformer monitoring while at the same time being substantially impermeable to transformer oils such as silicone oils and hydrocarbon oils. Data comparing the permeability of a PFDD polymer membrane against that of a conventional fluoropolymer, namely polytetrafluoroethylene ("PTFE"), is provided in Table I (for the instance in which the feed chamber contains gas):

Table I Permeabilities of Fluoropolymer Membranes to Various Gases			
Gas	Permeability (centiBarrer (cB))		
	Teflon AF-1600 ^(a)	Teflon AF-2400 ^(a)	Teflon PTFE ^(a)
Carbon dioxide		280,00	1,200
Hydrogen		220,000	980
Oxygen	34,000	99,000	420
Nitrogen		49,000	140
Ethylene		35,000	
Methane		34,000	
Ethane		18,000	

^(a) Teflon AF 1600 and Teflon AF 2400 are PFDD polymers while Teflon PTFE is a conventional tetrafluoroethylene polymer; all from E.I. Du Pont de Nemours and Company

Further, this high permeability is maintained even when the gases are dissolved in oil, as shown by the data in Table II (i.e., the feed chamber contains gas dissolved in oil):

Table II Permeabilities of Fluoropolymer Membranes to Various Gases Dissolved in Oil ^(a)			
Gas	Permeability (Barrer (B))		
	Teflon PTFE	Teflon AF-1600	Ratio AF 1600/PTFE
Helium	38	180	4.74
Hydrogen	19	200	10.53
Carbon dioxide	13	330	25.38
Oxygen	6.6	150	22.73
Nitrogen	2.7	57	21.11
Acetylene	3.5	53	15.14
Carbon monoxide	2.2	56	25.45
Methane	1.7	22	12.94
Ethylene	1.3	29	22.31
Ethane	1.3	24	18.46

^(a) Voltesso 35 hydrocarbon oil from Shell Oil.

However, those skilled in the art will appreciate that the present invention is not limited in its utility to the separation of gases dissolved in transformer oil and that it has general applicability to the separation of gases from other liquids. In addition to transformer oils such as silicone or hydrocarbon oil, the invention can be practiced with a wide variety of other liquids, subject only to the caveat that the liquid not be one which attacks or dissolves the permselective membrane or one which can permeate thereacross, such as hexane.

The foregoing detailed description of the invention includes passages which are chiefly or exclusively concerned with particular parts or aspects of the invention. It is to be understood that this is for clarity and convenience, that a particular feature may be relevant in more than just the passage in which it is disclosed, and that the disclosure herein includes all the appropriate combinations of information found in the different passages. Similarly, although the various figures and descriptions herein relate to specific embodiments of the invention, it is to be understood that where a specific feature is disclosed in the context of a particular figure, such feature can also be used, to the extent appropriate, in the context of another figure, in combination with another feature, or in the invention in general.

Further, while the present invention has been particularly described in terms of certain preferred embodiments, the invention is not limited to such preferred embodiments. Rather, the scope of the invention is defined by the appended claims.

What is claimed is:

1. A method of extracting dissolved gas from a gas-containing liquid, comprising the steps of
 - 5 (a) providing a separation cell having a permselective membrane comprising an amorphous perfluoro-2,2-dimethyl-1,3-dioxole polymer, the membrane partitioning the cell into a feed chamber and a permeate chamber;
 - (b) introducing into the feed chamber a gas-containing liquid to which the membrane is substantially impermeable, the gas-containing liquid having at
10 least one gas dissolved therein;
 - (c) permitting the at least one gas to permeate across the membrane from the feed chamber to the permeate chamber; and
 - (d) removing the at least one gas from the permeate chamber.
- 15 2. A method according to claim 1, wherein the gas-containing liquid is a hydrocarbon oil or a silicone oil.
3. A method according to claim 1, wherein the at least one gas is selected from the group consisting of carbon monoxide, carbon dioxide, hydrogen, water vapor,
20 methane, ethane, ethylene, and acetylene.
4. A method according to claim 1, wherein the at least one gas is a combination of at least each of carbon monoxide, carbon dioxide, hydrogen, methane, ethane, ethylene, and acetylene.
- 25 5. A method according to claim 1, wherein the perfluoro-2,2-dimethyl-1,3-dioxole polymer is perfluoro-2,2-dimethyl-1,3-dioxole homopolymer.
6. A method according to claim 1, wherein the perfluoro-2,2-dimethyl-1,3-dioxole
30 polymer is a copolymer of perfluoro-2,2-dimethyl-1,3-dioxole and at least one

comonomer selected from the group consisting of tetrafluoroethylene, perfluoromethyl vinyl ether, vinylidene fluoride, and chlorotrifluoroethylene; the perfluoro-2,2-dimethyl-1,3-dioxole constituting between 65 and 99 mole % of the copolymer.

- 5 7. A method according to claim 1, wherein the permselective membrane is a composite
membrane in which a layer of an amorphous perfluoro-2,2-dimethyl-1,3-dioxole
polymer is supported on a porous support material.
8. A method according to claim 7, wherein the support material is made of vinylidene
10 difluoride homopolymer or copolymer.
9. A method according to claim 1, wherein the permselective membrane is in the form
of a hollow tube.

* * * * *

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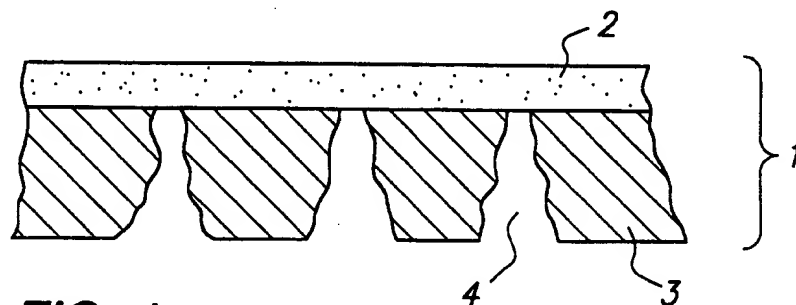


FIG. 1

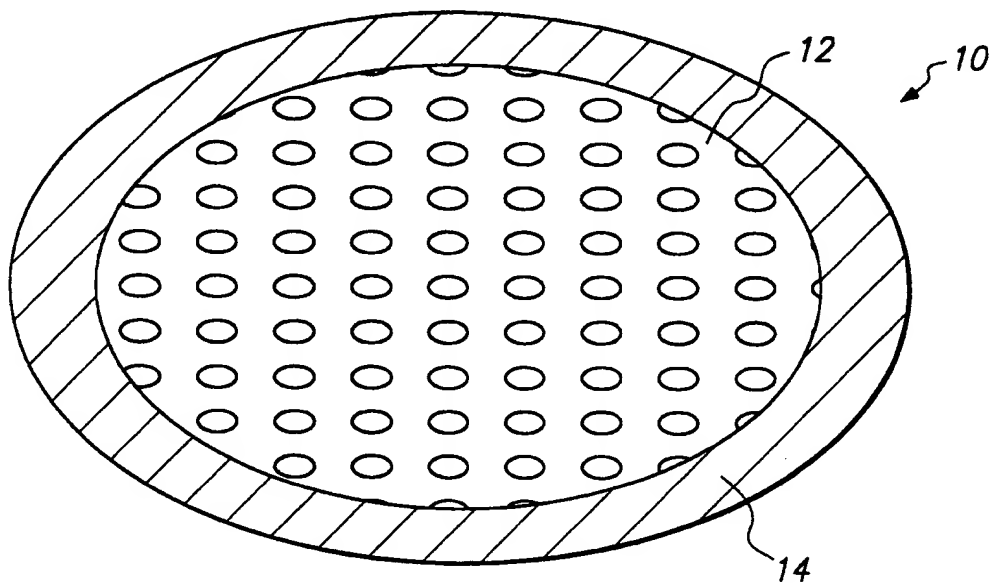


FIG. 2

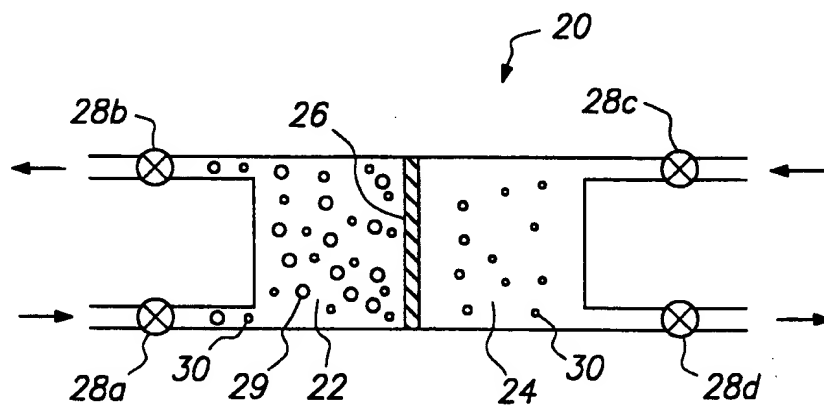
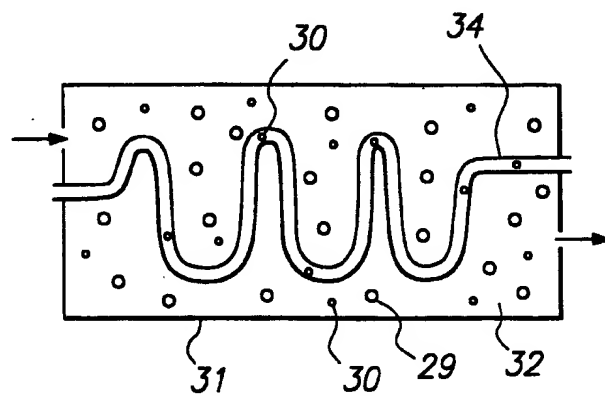
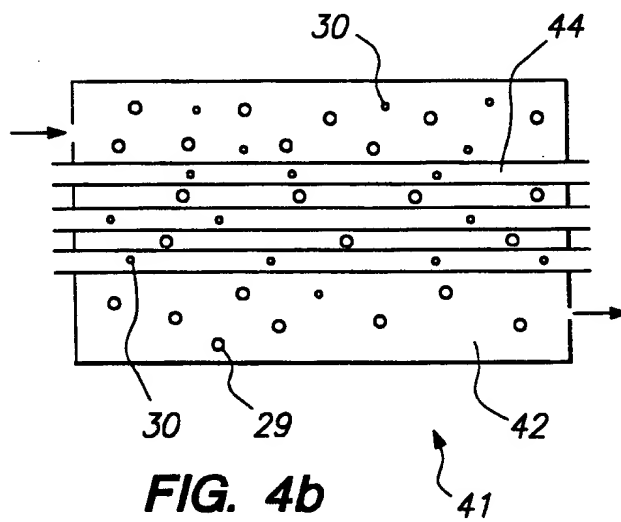


FIG. 3

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**FIG. 4a****FIG. 4b**

INTERNATIONAL SEARCH REPORT

National Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01D19/00 B01D69/10 B01D71/44

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01D C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 376 638 A (JAPAN GORE-TEX, INC.) 4 July 1990 see claim 1; figure 1 ---	1,9
A	WO 92 09353 A (W.L.GORE&ASSOCIATES, INC.) 11 June 1992 see claims 1,5 --- -/--	5-7,9

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 073 087 A (E.I.DU PONT DE NEMOURS AND COMPANY) 2 March 1983 see claim 1 & US 4 948 851 A cited in the application & US 4 975 505 A cited in the application & US 4 999 248 A cited in the application & US 5 006 382 A cited in the application -----	7
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/01972

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Information on patent family members

PCT/US 98/01972

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